TAMS

CONFIDENTIAL DRAFT MEMORANDUM

To	OLP BERA Team	Location	Various	Date	Sept. 17, 2002
From	Helen Chernoff	Location	TAMS	Job No.	
Subject	BERA Rewrite Mercury Methylation in Wetlands Ratio				

Based on the agency comments received on the draft of Chapter 8 of the BERA, the issue of mercury methylation was examined by TAMS with input from Chuck Merkel (USFWS) and Rebecca Quail (NYSDEC).

The first step was to try and obtain site-specific information for Onondaga Lake. Charles W. Sharpe and Charles Driscoll at Syracuse University had presented a poster at the Onondaga Lake Scientific Forum (November, 2000) entitled Mercury Dynamics in Onondaga Lake and Adjacent Wetlands. The poster abstract stated that: "The percentage of HgT that occurred as MeHg displayed a similar range between the water column and the wetland sites. Methyl Hg concentrations were between 0 percent and 96 percent of the HgT available, with one wetland site averaging 70 percent HgT as MeHg. The temporal patterns of the percentage of HgT occurring as MeHg were also highly variable." However, Charles Sharpe's thesis only measured total and methylmercury in the water column of Onondaga Lake wetlands and Dr. Driscoll knew of no studies that measured methylmercury in wetland sediments (solid phase). He suggested checking with Jim Sutherland of NYSDEC to see if they had any data. Jim Sutherland did collect some soils at several locations along the old bike path on the west side of the lake (which has since been paved), but the data were only total mercury.

The Onondaga Lake database was searched for appropriate data and sediment data from the lake from Phase 2A sampling in 2000 and from the 1995 and 1996 LCP Bridge Street sampling were found (see Tables 1 and 2, attached). In Onondaga Lake surface soil samples from 2000 where both total mercury and methylmercury were analyzed, total mercury ranged from 0.7 to 78 mg/kg in sediments and methylmercury comprised between 0.05 and 0.47 percent of the total mercury with an average of 0.17 percent (Table 1). The average total mercury concentrations in the lake sediment was 10 mg/kg. There was no obvious trend between depth or location of sediments.

At the LCP Bridge Street site, methylmercury comprised between 0.003 and 2.2 percent of the total mercury found in sediment with an average of 0.25 percent (Table 2). Total mercury concentrations were higher than in the lake sediments with an average of 32 mg/kg. The highest proportion of methylmercury was generally seen in samples with lower concentrations of total mercury (e.g., 3 mg/kg or less).

Because no methylmercury data were available for Onondaga Lake wetlands, the literature was reviewed for wetland methylation values. Zillioux et al. (1993) cited methylmercury comprising between 2 and 14 percent of total mercury in acidic Swedish bogs. Methylmercury ranged from

about 1 to 10 percent in US wetlands as measured by the USGS (Krabbenhoft et al., 1999). Krabbenhoft et al. found mining and urban areas to have the lowest methylation efficiency. Methylmercury production appeared proportional to total mercury concentrations at low sediment concentrations, but at high concentrations (1 ppm) little additional methylmercury was produced with increasing mercury. This appear to be applicable to Onondaga sediments, as the two lake stations with mercury concentrations less than 1 ppm (S342 and S365) had the highest percentage of methylmercury (Table 1) and a similar trend was seen in LCP Bridge Street sediments (Table 2).

Gilmour et al. (1998) studied mercury methylation in wetlands in the Florida Everglades. Methylation rates averaged between about 0.1 and 2 percent. The highest rates were seen in southern wetlands with lower nutrient concentrations, sulfate, and sulfide concentrations, which also had higher total mercury concentrations (up to about 0.4 ppm). The increase in methylmercury was considered to be driven by factors other than total mercury, because methylmercury concentrations increased by a factor of about 25, while total mercury increased only by a factor of 3 to 4.

Onondaga Lake is an eutrophic system with high sulfide concentrations (sulfide inhibits MeHg production), and is likely to have a wetland mercury methylation rate of less than 1 percent, similar to the eutrophic sites studied in the Florida Everglades. In addition, average mercury concentrations for all Onondaga Lake wetlands, except SYW-12 at the mouth of Ley Creek, were greater than 1 ppm and upper bound concentrations were all greater than 1.5 ppm (Table 3).

Based on the literature and measurements made on Onondaga Lake sediments, a mercury methylation rate of 1 percent is proposed for Onondaga Lake wetland soils[1]. This rate is considered to be protective of the Onondaga Lake ecosystem and would be used in the food-web model to estimate wildlife exposure to methylmercury. Hazard quotients for receptors with exposure to wetlands soil or prey (i.e., red-tailed hawk, mink, and short-tailed shrew) would be recalculated considering one percent of all mercury detected in wetland soils to be methylmercury and the remaining 99 percent would be considered to be inorganic mercury. Separate total mercury and methylmercury risks for the red-tailed hawk and short-tailed shrew will be calculated using separate toxicity values (note that the mink is already exposed to methylmercury through fish and invertebrate prey).

[1] Risks contained in the current draft of the BERA are based on zero percent methylmercury in wetland soils.

References:

Gilmour, C.C., G.S. Riedel, M.C. Ederlington, J.T. Bell, J.M. Beniot, G.A. Gill, and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the Northern Everglades. Biogeochemistry, 40:326-346.

Krabbenhoft D.P. , J.G. Wiener, W.G. Brumbaugh, M.L. Olson, J.F. DeWild, and T. J. Sabin. 1999. A National Pilot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients. USGS Toxic Substances Hydrology Program. Proceedings of the Technical Meetings. Charleston, SC. Water Res. Invest. Report. 99-4018 B. pp 147-160.

Zillioux, E.J, D.B. Procella and J.M. Benoit. 1993. Mercury cycling and effects in freshwater wetland ecosystems. Environmental Toxicology and Chemistry. 12: 2245-2264.

Table 1. Comparison of Total Mercury and Methylmercury Sediment Concentrations in Onondaga Lake

Survey Station	Sample Location	Sampling Date	Upper Depth (cm)	Lower Depth (cm)	Approx. Water Depth of Station (m)	Total Mercury (mg/kg dw)	Methylmercury (ug/kg dw)	MeHg/Hg Percent	Total Organic Carbon (% dry)
S372	NE corner of lake	8/11/00	0	15	1.5	1.6	2.9	0.18%	8.72
S332	off I-690 Storm Drain	8/11/00	0	15	3	3.0	3.8	0.13%	9.08
S305	off NMC	8/12/00	0	15	4	2.5	3.7	0.15%	5.51
S317	off Metro	8/11/00	0	15	4	17.2	8.1	0.05%	8.58
S323	off Ley Creek	8/13/00	0	15	4	1.6	3.9	0.24%	8.64
S344	off East Flume/SYW-19	8/10/00	0	15	4	77.7	120.6	0.16%	11.7
S337	off I-690 Storm Drain	8/11/00	0	15	4.5	15.4	15.3	0.10%	8.10
S315	off Metro	8/11/00	0	15	7	9.6	5.5	0.06%	7.96
S342	off East Flume	8/10/00	0	15	7	0.7	3.2	0.47%	3.60
S365	N. of Trib 5A	8/13/00	0	15	8	0.7	2.1	0.32%	7.68
S302	off NMC	8/12/00	0	15	9	3.0	2.1	0.07%	5.55
S320	off SYW-12/Ley Creek	8/13/00	0	15	9	6.1	10.2	0.17%	6.75
S303	off NMC	8/12/00	0	15	16.5	3.2	2.3	0.07%	6.29
S355	South Basin	8/10/00	0	15	16.5	3.0	6.7	0.22%	8.09
S354	btw. East F. & I-690 Drain	8/10/00	0	15	17	3.3	6.8	0.21%	7.32
		Overall Average				9.9	13.1	0.17%	7.6
		0 to 3 m				2.3	3.4	0.16%	8.9
		3 to 6 m				22.9	30.3	0.14%	8.5
		6 to 9 m				4.0	4.6	0.22%	6.3
		0 to 9 m				11.6	15.1	0.17%	7.7
		> 9 m				3.2	5.3	0.17%	7.2

Table 2. Mercury:Methylmercury Ratio in Sediment Collected at the LCP Bridge Street Site

Survey Station	Depth (cm)	Sampling Date	Sample Location	Log Notes (location characteristics)
DW12	0 - 6	10/02/95	West Flume to north of property boundary	marsh vegetated
DW13	0 - 6	10/02/95	West Flume to east of property boundary	flume
SD11	0 - 6	10/02/95	West Flume at Geddes Brook	marsh vegetated
DW03	0 - 6	10/04/95	Mouth of west ditch at ponded area	veg. ditch approx 1 in. deep
DW04	0 - 6	10/04/95	Mouth of east ditch at West Flume	veg. ditch approx 3-4 in deep
DW05	0 - 6	10/04/95	East ditch	grassy ditch
DW06	0 - 6	10/04/95	East ditch	ditch in marsh
DW07	0 - 6	10/04/95	Ponded area	unvegetated ditch
DW08	0 - 6	10/04/95	Ponded area	unvegetated ditch
DW09	0 - 6	10/04/95	Ponded area	vegetated ditch
DW15	0 - 6	10/04/95	On-site drainage ditch to east of west ditch	approx 4 - 6 in deep
DW16	0 - 6	10/04/95	On-site drainage ditch to east of west ditch	approx 8 in deep
SD02	0 - 6	10/04/95	West ditch	veg. ditch less than 1 in deep
SD10	0 - 6	10/04/95	Ponded area at West Flume	veg. marsh approx 2 in deep
SD14	0 - 6	10/04/95	Ditch by west plant wall	lined ditch
SD15	0 - 15	10/07/96	Ponded area, by west property boundary	vegetated, approx 0.5 ft deep
SD16	0 - 15	10/07/96	Ponded area, by west property boundary	center of ponded area, approx 4 in
SD17	0 - 15	10/07/96	Ponded area	vegetated approx 4 in deep
SD18	0 - 15	10/07/96	East ditch	vegetated, approx 3 in deep
SD19	0 - 15	10/07/96	Ponded area	vegetated, approx 4 in deep
SD20	0 - 15	10/07/96	Ponded area	vegetated, approx 3 in deep
SD21	0 - 15	10/07/96	Ponded area	vegetated, approx 4 in deep
SD22	0 - 15	10/07/96	Ponded area	vegetated, very moist, no water
SD23	0 - 15	10/07/96	Ponded area	vegetated moist area, no water
SD24	0 - 15	10/07/96	Ponded area	vegetated moist area, no water
SD25	0 - 15	10/07/96	Ponded area	vegetated moist area, no water
SD26	0 - 15	10/08/96	West Flume west of property boundary	vegetated, approx 2 in deep
SD27	0 - 15	10/08/96	West Flume west of property boundary	vegetated moist area, no water
SD28	0 - 15	10/08/96	West Flume west of property boundary	vegetated moist area, no water

Notes:

J indicates an estimated value. Max. Conc.

Stations designated as "DW" in database are believed to be "SD" (sediment) stations. Min. Conc.

Sampling conducted by Parsons Engineering Science, Inc. Ave. Conc.

Total Mercury (mg/kg dw)	Methyl-mercury (ug/kg dw)	MeHg/Hg Percent
23.0 J	11.0 J	0.048%
0.6	1.2 J	0.215%
28.6 J	7.8 J	0.027%
35.8	13.3 J	0.037%
4.4	5.2	0.118%
24.2 J	15.9 J	0.066%
1.8	3.8	0.211%
51.5	13.2	0.026%
131.0 J	14.6	0.011%
10.2 J	11.5 J	0.113%
57.7 J	26.3	0.046%
193.0 J	175.0 J	0.091%
29.8	15.8 J	0.053%
56.0	3.6 J	0.006%
2.9	63.8	2.200%
56.3 J	14.0 J	0.025%
56.4 J	11.4 J	0.020%
9.3 J	3.8	0.041%
9.5 J	29.7	0.313%
21.5 J	19.4	0.090%
41.9 J	1.2	0.003%
7.5 J	2.4	0.031%
12.6 J	74.3	0.590%
1.8 J	20.1	1.117%
1.5 J	6.2	0.414%
1.7 J	12.2	0.718%
11.5 J	14.6 J	0.127%
18.5 J	31.7 J	0.171%
23.3 J	68.9 J	0.296%
193	74	2.200%
0.6	1.2	0.003%
32	25	0.249%

Table 3. Onondaga Lake Wetlands and Dredge Spoils Mercury Exposure Concentrations

Location	Detection Frequency	Minimum (mg/kg)	Maximum (mg/kg)	Arithmetic Mean (mg/kg)
SYW-19 (Wetland at the Mouth of Harbor Brook)	4/4	4.8	25	15
SYW-12 (Wetland at the Mouth of Ley Creek)	3/4	5.4E-02	1.5	0.7
SYW-10 (Wetland at the Mouth of Ninemile Creek)	4/4	1.2	3.4	2.1
SYW-6 (Northwest Wetland Area)	4/4	0.2	3.9	1.4
Dredge Spoils (surface samples)	7/8	5.4E-02	4.0	0.6

Notes:
Maximum concentration used for upper bound exposure point concentration (EPC) since 95% UCL is generally (for sample sizes of 10 or more.

Upper Bound EPC (mg/kg)
25 Max
1.5 Max
3.4 Max
3.9 Max
4.0 Max

calculated